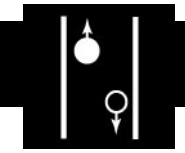
FLOTATION



Bubble–Particle Adherence: Synergistic Effect of Reagents

B. J. Bradshaw and C. T. O'Connor, University of Cape Town, Rondebosch, South Africa

Copyright © 2000 Academic Press

Introduction

It is well known in the practice of flotation that mixtures of various collectors often behave with greater effectiveness than would be expected from their individual known characteristics. This phenomenon is a classical example of synergism in flotation, in which the combined effect exceeds the sum of the linearly weighted partial effects. Such phenomena are not only consciously applied by adding mixtures of reagents, especially collectors, but may also occur inadvertently since many industrial reagents are synthesized from less than absolutely pure chemicals, resulting in the presence of small amounts of different product molecules which are often capable of having a positive synergistic effect on the flotation behaviour. Such synergism can have a significant effect not only on the recovery but also on the selectivity of specific minerals in differential flotation. The manner in which reagents interact in order to achieve a synergistic effect is a complex function of their chemical nature as well as their chemisorptive or physisorptive properties. The former will determine whether the chemical composition of the reagent changes when another compound is present through, for example, a dimerization reaction. The latter will determine how competitive or synergistic adsorption will influence the ultimate flotation behaviour. The analysis of synergism between reagents in flotation is complicated by the fact that the roles and interactions of the different classes of reagents are difficult to isolate due to the complexity of the flotation process, viz. the frother is added to stabilize the froth zone but can also interact with the collector and affect the performance of the collection zone.

This review firstly discusses those properties of pure collectors, frothers, depressants and activators which are pertinent to their potential synergistic behaviour. The interactions between collectors, frothers and each other are then reviewed. The emphasis here is on sulfide minerals but similar effects have been extensively reported in the case of oxide flotation. Finally, an hypothesis is proposed to explain the synergism observed when mixtures of thiol collectors are used in the flotation of pyrite. This represents a typical sulfide mineral flotation system and will serve to highlight how the various subprocesses of flotation may be influenced in a synergistic manner, thus influencing the ultimate flotation performance.

Functional Roles of Pure Reagents

Collectors

The predominant functional role of collectors is to induce hydrophobicity by adsorption onto the desired mineral and they are therefore concentrated at the mineral–water interface. Collectors are heteropolar molecules containing a nonpolar hydrocarbon chain, which renders the particle hydrophobic, and a polar group that interacts with the mineral surface.

Collector molecules can be divided into three classes: nonionic, which are largely insoluble and used in the flotation of coal and graphite; cationic, which are typically amine salts and used in the flotation of silicates and sulfides at alkaline conditions; and anionic, which are used to float basic minerals such as metal oxides and sulfides. Fatty acids are used for the flotation of nonsulfide minerals such as apatite, calcite, feldspar and hematite. Sulfonates and sulfates are used for apatite as their frothing properties limit their usefulness for other systems. Sulfhydryl or thiol collectors are used for the flotation of sulfide minerals and, of these, xanthates, first patented in 1925, are still the most widely used.

The mechanism of mineral–collector bonding depends on the collector type and the nature and charge of the mineral surface and can occur via physisorption or chemical bonding. There are several modes of chemical interaction of the collector with the mineral surface. In the case of physisorption, the collector does not interact with the mineral surface. The attachment is due primarily to van der Waals forces and the Gibbs free energy of adsorption is relatively low. In the case of chemisorption, when the collector interacts with the mineral surface without movement of the metal ions from their lattice sites, this produces

DropBooks

monolayer coverage. When the surface chemical reactions are associated with movement of metal ions from their lattice sites, multilayers may form. If a reaction occurs in the bulk solution between dissolved ions and the collector, a hydrophobic surface will only be established if there is bulk precipitation on the mineral surface.

Sulfide minerals are semiconductors and react electrochemically with thiol collectors according to the mixed potential model. This involves the cathodic reduction of oxygen and the anodic oxidation of collectors. The electrochemical potential of the system and the thermodynamics of the respective reactions determine the nature of the surface products. Depending on the nature of the surface products formed, the collector may however be physisorbed, such as in the case of the neutral dithiolate, or chemisorbed, as in the case of the metal thiolate. Naturally, when mixtures of collectors are used, a combination of these mechanisms and products may occur, possibly resulting in an enhanced flotation performance.

Frothers

Frothers are added to create a stable dispersion of bubbles in the pulp which will subsequently create a reasonably stable froth and which will allow selective drainage from the froth of entrained gangue and improve the flotation selectivity. The frother also affects the flotation kinetics. They are nonionic heteropolar molecules and, unlike collectors, are not associated with particular categories of minerals. The frothing ability of a compound is associated with hydroxyl (–OH), ester (–COOR) and carbonyl (–CO) chemical groups, and commercial frothers can be divided into three main categories: alcohols, alkoxyparaffins, polyglycols and polyglycol ethers. The polar end of the frother molecule forms hydrogen bonds with the water and no mineral–frother bonds are formed. The nonpolar end is hydrophobic so that the frother concentrates at the air–water interface and is thus described as being surface-active. This affects the surface tension, which indicates the difference between the surface activity of frothers and causes a stable froth to form. In general, increased surface activity results in increased floatability and froth stability.

Depressants

The role of depressants, which are either inorganic salts, such as sodium silicate, sodium sulfite or organic compounds such as polysaccharides, dextrin and starch derivatives, guar gums, carboxymethylcel lulose and alginates, is to reduce the collection of unwanted gangue which consists of typically talcaceous or other oxide minerals. This is done by either enhancing the hydrophilic nature of the gangue surface, by preventing the formation of hydrophobic species which might adsorb on the gangue surface or by preventing the coating of unwanted slimes on the mineral surface. Mechanisms of depression also include the formation of large aggregates and the complexation of the collector in solution.

Activators

Activators are specifically added to enhance flotation performance, usually by modifying the surface of the particle in some way so as to make it more amenable to interaction with the collector. They may however have unexpected effects, for example, by complexing with other ions in solution and rendering particles less floatable. Copper sulfate, for example, is a well-known activator. Under certain circumstances, in sulfide flotation, the copper may ion-exchange with surface ions, creating a readily floatable particle but in different pulp conditions may complex as a hydroxy species and depress the particles. Such effects may be considered synergistic but fall outside the scope of this article. Another commonly used activator is sodium sulfide or bisulfide which is used as a sulfidizing reagent for tarnished or oxidized ores.

Synergistic Interactions Between Reagents

There has been a considerable amount of work done on the effects of mixing reagents in flotation. **Table 1** summarizes much of this literature with respect to type of reagents mixed, minerals tested, measurements made and the benefits observed.

Collector–Collector Interactions

The use of mixtures of collectors has long been recognized in plant practice and has been shown to enhance flotation performance. These benefits have been reported for a wide range of collector mixtures (anionic, cationic and nonionic) and include lower dosage requirements, improved selectivity and rates and extents of recovery and an increase in the recovery of coarse particles. In many cases an optimum ratio of constituent collectors was shown to exist. Dithiophosphates are a class of thiol collectors that are so widely used in mixtures that they are known as promoters.

Using measurements obtained from experimental techniques shown in Table 1, a number of mechanisms have been proposed by various authors to

Table 1 The effects of mixing reagents in Flotation

Interactions	*Reagents*[a] *(ratios tested)*[b]	*Mineral systems*[c]	*Techniques*	*Benefit of mixture*	*Reference*
Collector : collector Thiol–thiol	Ethyl X : amyl X (2 : 1, 1 : 2 mass)	Arsenopyrite (P)	Batch flotation	Higher rates of recovery with mixtures. Optimum mixtures: ethyl X : amyl X (1 : 2) for arsenopyrite and (1 : 1) for galena	Plaskin *et al.* (1954)
	Ethyl X : amyl X : diethyl DTP (1 : 1 mass)	Arsenopyrite (P)			
	Ethyl X : butyl X : diethyl DTP (1 : 1 mass)	Galena (P)	Radiographic adsorption techniques	More even collector coverage on mineral surface with mixture	Plaskin and Zaitseva (1960)
	n-propyl DTC : *n*-hexyl DTC : cyclohexyl DTC : di propyl DTC (10 : 90; 50 : 50; 90 : 10)	Pyrite ore with quartz gangue (South Africa) (1.27% Sulfur)	Batch flotation	Increased recoveries for all mixtures. Optimum ratio: *n*-propyl DTC : cyclohexyl DTC (90 : 10)	Bradshaw and O'Connor (1994)
	Butyl X : butyl DTP (50 : 50)	Galena (P)	Adsorption Bubble pick-up	Preferential DTP adsorption from mixture with no increased mass picked up by bubble	Wakamatsu and Numata (1979)
	Isopropyl DTC : iso propyl X (1 : 2 mass)	Chalcopyrite ore (Canada) (1.1% Cu)	Batch flotation	Better results with DTC : X mixture than with pure DTC	Falvey (1969)
	Di-isobutyl DTP : iso butyl X (30 : 70; 50 : 50; 70 : 30 mass)	Platinum group metal (PGM) ore	Batch flotation	Recovery improved from 73.2% for pure X to 80% with 70 : 30 mixture	Mingione (1984)
	Di-isobutyl DTP : SMBT (50 : 50 mass)	Auriferous pyrite ore (0.38 g/t Au, 1% Sulfur)		Recovery improved from 73.8% for pure SMBT to 79.9% with mixture	
	Di-isobutyl DTP : SMBT (50 : 50; mass)	Sphalerite ore (1.5% Zn)		Recovery improved from 90% for pure SMBT to 95% with mixture	
	Isobutyl X : cyano diethyl DTC (12 : 44 mass)	Chalcopyrite/pyrite with quartz gangue (China)	Batch flotation	Chalcopyrite recovery increased from 92.4% to 92.8% with 12 : 44 mixture	Jiwu *et al.* (1984)
	DTP : MTP (types unspecified) (75 : 25; 50 : 50; 25 : 75)	Mixed copper sulfide ore	Batch flotation	Optimum recovery at 75 : 25 due to combination of collector properties	Mitrofanov *et al.* (1985)

DropBooks

Table 1 *Continued*

Interactions	*Reagents*[a] *(ratios tested)*[b]	*Mineral systems*[c]	*Techniques*	*Benefit of mixture*	*Reference*
	Ethyl X : di-ethyl DTC (80 : 20; 66 : 33; 50 : 50; 33 : 66; 20 : 80)	Hazelwoodite (SP)	Adsorption Surface tension Microflotation	Optimum ratio: 33 : 66 for lower surface tension, increased microflotation recovery and extent of adsorption	Critchley and Riaz (1991)
	SMBT : amyl X (70 : 25 mass)	Gold and arsenopyrite ore (France)	Batch flotation	Gold and arsenopyrite recovery increased with use of mixture	Van Lierde and Lesoille (1991)
Collector : collector Thiol–thiol	Isopropyl X : dicresyl DTP (95 : 5)	Mixed copper sulfide/ oxide ore (2.9% Cu)	Batch flotation	Enhanced rate and recovery with mixture. Recovery from 80–83% Cu	Adkins and Pearse (1992)
	n-butyl X : cyclohexyl DTC (95 : 5; 90 : 10; 85 : 15; 50 : 50)	Pyrite ore with quartz gangue (South Africa) (0.83% S)	Batch flotation	Recovery increased for all mixtures. Highest recovery for 50 : 50 mixture	Bradshaw and O'Connor (1997)
	n-butyl X : cyclohexyl DTC (90 : 10)	Pyrite (P)	Bubble loading Thermochemical	Increased bubble loading and heat of adsorption with mixture	
Thiol–anionic	Ethyl X : sodium oleate (10 : 90; 20 : 80; 40 : 60; 60 : 40; 80 : 20)	Pyrite (polished section) Gold (polished section)	Surface tension Contact angle	Largest contact angle corresponded to low surface tension with 3 : 1 mixture	Valdiviezo and Oliveira (1993)
Thiol–anionic polymers	Ethyl X : amino acid glycine (1 : 1)	Chalcocite (P), galena (P), pyrite (P)	Microflotation	Higher recoveries obtained for all sulfides with mixture	Hanson *et al.* (1988)
	Butyl X : hydrolysed polyacrylamide (90 : 10)	Mixed sulfide ore with gold	Batch flotation	90 : 10 mixture increased gold recovery 3% above that obtained with pure X	Orel *et al.* (1986)
Thiol–cationic	Ethyl X : ammonium bromide (05 : 1; 1 : 1; 2 : 1; 4 : 1)	Pyrite (P), quartz (P)	Surface tension Microflotation	Lowest surface tension for 1 : 1 mixture Increased recovery with all mixtures	Buckenham and Schulman (1963)
Collector : frother	Ethyl X : alkyl alcohols	Chalcocite (P)	Frothability	Enhanced frothability with X added to alcohols	Leja and Schulman (1954)
	Ethyl X : α-terpinol	Chalcocite (P)	Microflotation Frothability	Increased recovery with increasing dosage of frother with xanthate. Only froths in 3 phase	Lekki and Laskowski (1971)

Table 1 *Continued*

Interactions	*Reagents[a] (ratios tested)[b]*	*Mineral systems[c]*	*Techniques*	*Benefit of mixture*	*Reference*
	Ethyl X : α-terpinol (1 : 1)	Chalcocite ore	Batch flotation	Increased recovery due to joint frother–collector interactions	Lekki and Laskowski (1975)
	Butyl X : 41G	Galena (polished section)	Contact angle	Contact angle on mineral increased with addition of frother to X	Harris (1982)
	Xanthogen formate : MIBC	Copper sulfide ore (Chile)	Batch flotation Plant practice	Collector dosage reduced 40% to achieve same recovery, which reduced cost and selectivity	Crozier and Klimpel (1989)
Collector : frother	Ethyl X : alkyl alcohols Range of molar concentrations	No mineral	Surface tension Film thickness	Reduced film thickness and surface tension with increasing addition of X	Manev and Pugh (1993)
Frother : frother	MIBC, pine oil, cresylic acid, PPG	Various copper sulfide ores	Plant practice	Survey of 66 plants showed 37% used mixtures of frothers	Crozier and Klimpel (1989)

[a]Reagents tested as components of the mixture are separated by a colon. Where more than two reagents are in the list, all the reagents listed have been tested at all the ratios specified in brackets.
[b]Ratios are mole ratios unless otherwise specified as mass ratios (mass).
[c]In cases where the origin or grade of the ore is not included in Table 1, this information was not available in the original reference. X, Xanthate class of reagents; DTC, dithiocarbamate class of reagents; DTP, dithiophosphate class of reagents; MTP, monothiophosphate class of reagents; SMBT, sodium mecaptobenzonthiazole; PPG, polypropylene glycol; 41G, a proprietary frother containing triethoxybutane manufactured by NCP; MIBC, methyl isobutyl carbinol; (P), pure mineral sample with no gangue component; (SP), synthetically prepared pure mineral sample.

explain the fact that the mixtures give a flotation performance greater than that expected from the contributions of each individual component. These proposals are based on effects related to adsorption of the collectors on the surface of the particle, interactions between the reagents, either in the bulk or at the surface, or changing froth characteristics.

When using mixtures of collectors it has often been observed that there is a greater surface coverage of the adsorbed collectors on the mineral than would have been expected from their weighted averages. This could either enhance the overall hydrophobicity of the mineral surface or result in an adsorbed surface layer of collector molecules more suitable for frother–collector interactions. The increased mineral hydrophobicity could result from the formation of a more evenly distributed surface species. The change in hydrophobicity can be measured by, for example, changes in contact angle, bubble loading and ultimately the recovery in batch flotation tests. It has also been proposed that, for certain systems, when a mixture of collectors is exposed sequentially to a surface which, by definition, must have a heterogeneous distribution of energetically different sites, the weaker collector will adsorb preferentially on the strong sites and the strongly adsorbing collector, added subsequently, will adsorb on the weaker sites. In this way as many sites as possible are utilized for adsorption, thus enhancing the hydrophobicity. Single collector addition may only result in adsorption on strongly adsorbing sites, forming nonuniform coverage and thus a less than optimal adsorption capacity. It is possible that such an effect will not be observed if the collectors are pre-mixed before addition, thus emphasizing the fact that synergism may depend on the sequence of addition as much as on the presence of a mixture.

The grade of the concentrate is largely a function of the depressant used, which affects the froth zone characteristics. The presence of hydrophobic solids in the froth phase will destabilize the froth, causing bubble coalescence in the froth which results in improved drainage and consequently increased selectivity and grades. The presence of hydrophilic or only

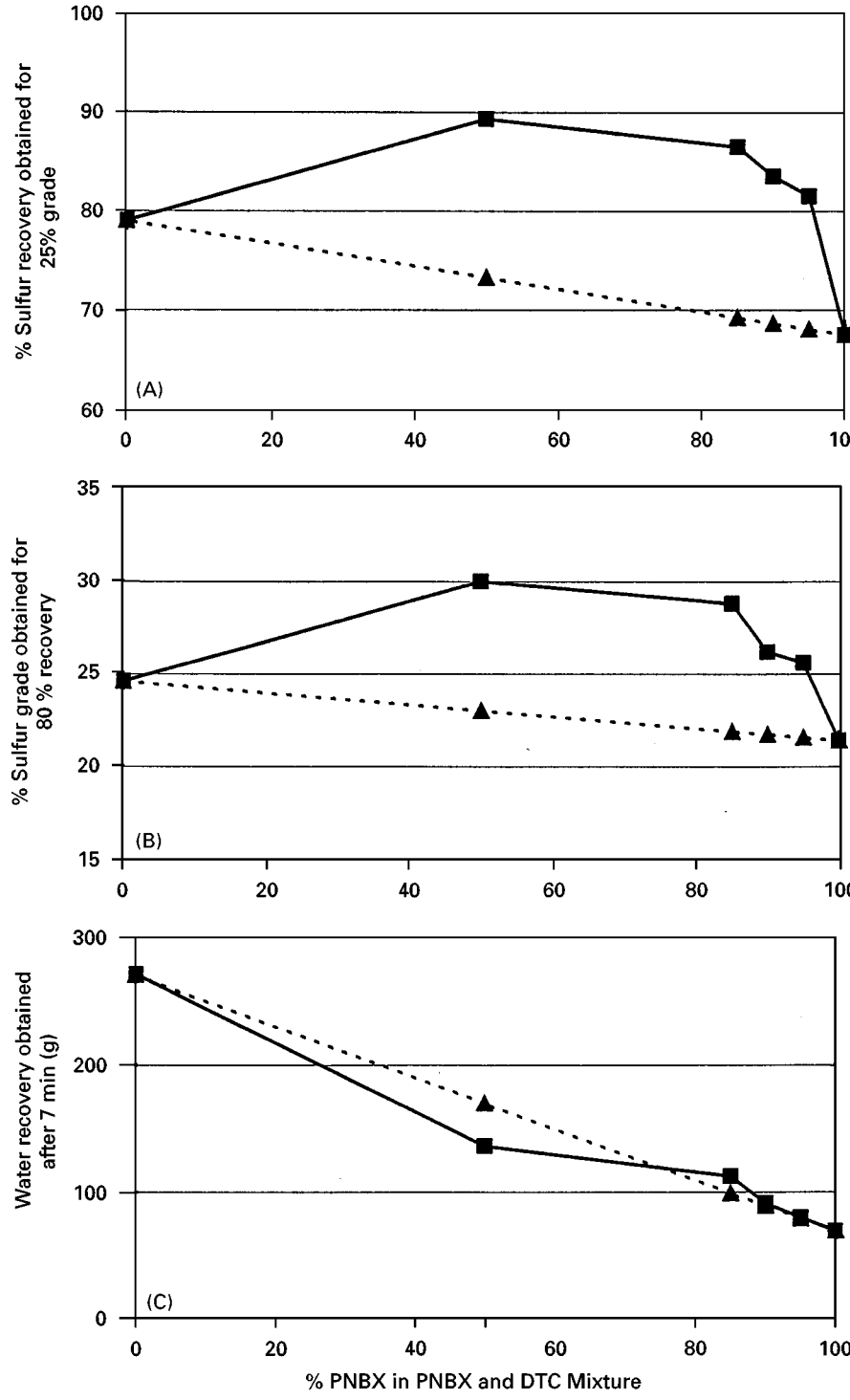


Figure 1 The effect of mixtures of collectors on batch flotation performance of a low-grade pyrite ore at pH 4. Values measured (squares) were compared with those predicted from the linearly additive mole ratio contribution of potassium *n*-butyl xanthate (PNBX) and dithiocarbamate class of reagents (DTC; triangles) for (A) % sulfur recovery obtained for 25% grade; (B) % sulfur grade obtained for 80% recovery; and (C) water recovery obtained after 7 min (g).

slightly hydrophobic minerals can stabilize the froth zone and thereby decrease the grade achieved. The use of a combination of collectors resulting in both physisorbed and chemisorbed surface products can also affect the froth structure and influence the final grade achieved. It is also often observed that

enhanced performance is achieved when a strong collector with no frothing properties is used with a weaker collector with frothing properties. The former increases coarse particle recovery and the latter increases fine particle recovery. This is however not a true synergistic effect since the combined effect is the sum of the individual effects.

Collector–Frother Interactions

Before the collision of a mineral particle and an air bubble, adsorbed layers of reagents are present at both interfaces. At the time of collision, there are interactions between these layers which are affected by the nature and charge of the respective molecules. Any associated molecules are anchored to the mineral group by the polar groups of the collector. The strength of this film determines the tenacity of attachment of the mineral to the bubble and the ultimate success of the flotation process. When the molecular associations between frother and collector are suitably balanced the appropriate mechanical properties of the film at the interface are created, resulting in good recoveries and grades. If the collector or frother dosages are too high, the molecules would be too densely packed and penetration and successful attachment would not take place. This supports the well-known phenomenon that too high a dosage of reagents can result in reduced recoveries. In this case synergistic interactions between the frother and collector that improved flotation performance at the lower dosages are no longer possible at the higher dosage.

Frother molecules can accumulate at the mineral surface, without enhancing its hydrophobicity and, at the time of collision with a bubble, re-orientate quickly, facilitating mineral–bubble attachment. this produces a stable three-phase froth and strong tenacity of mineral–bubble attachment. An alternative explanation is that at the mineral–water interface the alkyl chains of frother and collector molecules are held together by van der Waals forces. Frothers are able to hydrogen-bond with the oxygen atom in the collector molecule. These associations are only formed when a mineral is present. The frother's ability to interact with the collector is thus more significant than its surface activity, which is required to produce a stable froth zone. This also explains why detergents are not suitable frothers. It has moreover often been shown that the collector can affect frothing properties and that the frother can affect mineral hydrophobicity.

The surface activity and thus frothability of the frother is very sensitive to the presence of small amounts of other substances, such as impurities or collector molecules. The chemical nature of certain combinations of frothers and collectors may result in interactions occurring at the point of collision of the pure components. The properties of frothers can sometimes be additive, with the mixing of stronger and weaker frothers to form medium-strength frothers.

DropBooks

Synergistic Interactions – A Case Study

Synergistic enhancement of flotation performance has been observed in batch flotation tests with a low

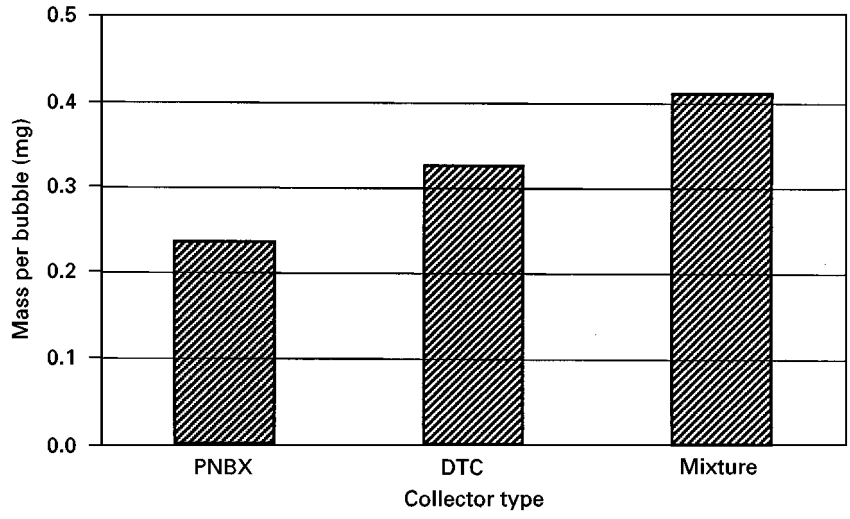


Figure 2 The mass loading per bubble for bubbles of average diameter of 1.2 mm of pyrite with equimolar amounts of potassium *n*-butyl xanthate (PNBX), dithiocarbamate class of reagents (DTC) and the 90 : 10 mixture of collectors added at pH 4.

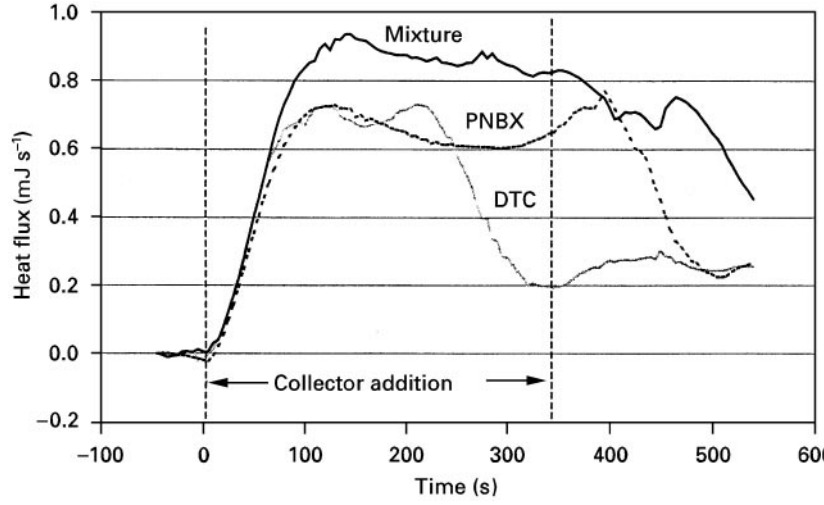


Figure 3 The difference in heat flux measured when equimolar amounts of potassium *n*-butyl xanthate (PNBX), dithiocarbamate class of reagents (DTC) and 90 : 10 mixture of collectors are added to pyrite at pH 4.

grade pyrite ore using thiol collectors at pH 4. The collectors tested were potassium *n*-butyl xanthate (PNBX) and an alkyl dithiocarbamate collector. Performance was analysed using grade-recovery data as well as water and mass recoveries and the rate of sulfur recovery. The froth surface was analysed using digital image analysis. In all experiments the total molar concentration of collector was constant.

Figure 1 shows the batch flotation results as represented by sulfur grade at 80% recovery, the sulfur recovery at 25% grade and the water recovery, all as a function of mole ratio of components. It is clear that the grades and recoveries are greater than would be expected from a merely linearly additive effect and are synergistically enhanced. Obviously pure collectors may not show linearity with respect to dosages but in the present case the dosages were in the range where these differences were minimal. The change in water recovery, however, was linearly proportional to the molar contribution of the components and clearly the synergistic effect was only influencing the behaviour of the solid particles. Digital image analysis of the froth showed that, when the mixture of collectors was used, the froth was more mobile and the froth surface bubble size was larger. This may be due to the frother–collector interactions, decreasing froth stability, increasing drainage of entrained material and increasing the grades obtained.

In order to elucidate the mechanisms of synergism, the extent of bubble loading and the heats of adsorption were measured for the respective collectors and collector mixtures using pure pyrite at pH 4, (Figure 1). **Figure 2** shows that, for bubbles of average diameter of 1.2 mm, increased bubble loading resulted from the use of a mixture of collectors and **Figure 3** shows that when a mixture of collectors was used there was a stronger adsorption than in the case of the pure xanthate, where multilayer adsorption of dixanthogen is indicated, and in the case of dithiocarbamate where pseudo-monolayer adsorption is indicated. In this example, the synergistic effect observed is attributed to increased mineral hydrophobicity, which is thought to be due to the weakly adsorbing dixanthogen adsorbing in multilayers around the strongly adsorbing dithiocarbamate, which acts as a sort of anchor on the surface of the mineral particle. The ultimate result is an increase in bubble loading, an improvement in froth characteristics and a greater grade and recovery.

Further Reading

Bradshaw DJ and O'Connor CT (1997) The synergism of mixtures of thiol collectors in the flotation of low grade pyrite ores. In: Hoberg H and von Blottnitz H (eds) *Proceedings of the XX International Minerals Processing Congress, Aachen*, vol. 3, pp. 343–354. Germany: GMBH Publishers.

Fuerstenau DW (1995) Where are we in flotation chemistry after 70 years of research? In: *Proceedings of the XIX International Minerals Processing Congress, San Francisco*, SME, vol. 3, pp. 3–18.

Harris PJ (1982) Frothing phenomena and froths. In: King RP (ed.) *Principles of Flotation*, pp. 237–250. Johannesburg: South African Institute of Min. Metall.

Klimpel RR and Hansen RD (1988) Frothers. In: Somasundaran P and Moudgil BM (eds) *Reagents in Mineral Technology*, pp. 387–409. New York: Marcel Dekker.

Laskowski JS (1993) Frothers and flotation froth. *Mineral Processing and Extraction Metall. Review* 12: 61–89.

Leja J (1989) Interactions of surfactants. *Mineral Processing and Extraction Metall. Review* 5: 1–22.

Leja J and Schulman JH (1954) Flotation theory: molecular interactions between frothers and collectors at solid–liquid interfaces. *Transactions of the A.I.M.E.* 199: 221–228.

Lekki J and Laskowski JS (1971) On the dynamic effect of frother–collector joint action in flotation. *Transactions of Institute of Min. Metall.* 80: C174–C180.

Mingione PA (1984) Use of dialkyl and diaryl dithiophosphate promoters as mineral flotation agents. In: Jones MJ and Oblatt R (eds) *Reagents in the Minerals Industry*, pp. 19–24. London: Inst. Min. Metall.

List of References from Table 1

Adkins SJ and Pearse MJ (1992) The influence of collector chemistry on the kinetics and selectivity in base metal sulfide flotation. *Mineral Engineering* 5: 295–310.

Bradshaw DJ and O'Connor CT (1994) The flotation of pyrite using mixtures of dithiocarbamates and other collectors. *Mineral Engineering* 7: 681–690.

Bradshaw DJ and O'Connor CT (1997) The synergism of mixtures of thiol collectors in the flotation of low grade pyrite ores. In: Hoberg H and von Blottnitz H (eds) *Proceedings of the XX International Minerals Processing Congress*, Aachen, vol. 3, pp. 343–354. Germany: GMDB Publishers.

Buckenham MH and Schulman JH (1963) Molecular association in flotation. *Transactions of the Institute of Mineral and Metallurgy* 7: C1–C6.

Critchley JK and Riaz M (1991) Study of synergism between xanthate and dithiocarbamate collectors in flotation of heazlewoodite. *Transactions of the Institute of Mineral and Metallurgy* 100: C55–C57.

Crozier RD and Klimpel R (1989) Frothers: plant practice. *Mineral Processing and Extractive Metallurgy Review* 5: 257–279.

Falvey JJ (1969) *Dialkyl Dithiocarbamate as Froth Flotation Collectors*. US patent no. 3 464 551.

Hanson JS, Barbaro M, Fuerstenau DW, Marabini A and Barbucci R (1988) Interaction of glycine and a glycine-based polymer with xanthate in relation to the flotation of sulfide minerals. *International Journal of Mineral Processing* 23: 123–135.

Harris PJ (1982) Frothing phenomena and froths. In: King RP (ed.) *Principles of Flotation*, pp. 237–250. Johannesburg: South African Institute of Mining and Metallurgy.

Jiwu M, Longling Y and Kuoxiong S (1984) Novel frother collectors for flotation of sulfide minerals–CEED. In: Jones MJ and Oblatt R (eds) *Reagents in the Minerals Industry*, pp. 287–290. London: Institute of Mining and Metallurgy.

Leja J and Schulman JH (1954) Flotation theory: molecular interactions between frothers and collectors at solid–liquid interfaces. *Transactions of the American Institute of Mining, Metallurgical and Petroleum Engineers* 199: 221–228.

Leja J (1989) Interactions of surfactants. *Mineral Processing and Extraction Metallurgy Review* 5: 1–22.

Lekki J and Laskowski JS (1971) On the dynamic effect of frother–collector joint action in flotation. *Transactions of the Institute of Mining and Metallurgy* 80: C174–C180.

Lekki J and Laskowski JS (1975) A new concept of frothing in flotation systems and general classification of flotation frothers. In: *Proceedings of the XI International Minerals Processing Congress*, Universita de Calgari, Calgari, pp. 427–448.

Manev E and Pugh RJ (1993) Frother/collector interactions in thin froth films and flotation. *Colloids and Surfaces* 70: 289–295.

Mingione PA (1984) Use of dialkyl and diaryl dithiophosphate promoters as mineral flotation agents. In: Jones MJ and Oblatt R (eds) *Reagents in the Minerals Industry*, pp. 19–24. London: Institute of Mining and Metallurgy.

Mitrofanov SI, Kuz'kin AS and Filimonov VN (1985) Theoretical and practical aspects of using combinations of collectors and frothing agents for sulphide flotation. 15e Congres International de Mineralurgie, vol. 2, pp. 65–73. St. Ettienne: Societe de l'Industrie Minerale et du Bureau de Recherches Geologiques et Mineres.

Orel MA, Chibisov VM and Lapatukhin IV (1986) Use of mixtures of butyl xanthate and hydrolyzed ployacrylamide when floating gold-containing ore. *Soviet Journal of Non-ferrous Metals* 27: 97–98.

Plaskin IN and Zaitseva SP (1960) Effect of the combined action of certain collectors on their distribution between galena particles in a flotation pulp. (Mintek translation no. 1295, June 1988.) Naachnye Soobshcheniya Institut Gonnogo dela Imeni AA Skochinskogo, Akademiya Nauk SSSR, Moskva, Report no. 6, pp. 15–20.

Plaskin IN, Glembotskii VA and Okolovich AM (1954) Investigations of the possible intensification of the flotation process using combinations of collectors. (Mintek translation Feb. 1989.) Naachnye Soobshcheniya Institut Gonnogo dela Imeni AA Skochinskogo, Akademiya Nauk SSSR, Report no. 1, pp. 213–224.

Valdiviezo E and Oliveria JF (1993) Synergism in aqueous solutions of surfactant mixtures and its effect on the hyrophobicity of mineral surfaces. *Mineral Engineering* 6: 655–661.

DropBooks

Van Lierde A and Lesoille M (1991) Compared effectiveness of xanthate and mercaptobenzothiazole as gold and arsenopyrite collectors. In: *Proceedings of the XVII International Minerals Processing Congress*, Dresden, vol. IV, pp. 111–119.

Wakamatsu T and Numata Y (1979) Fundamental study on the flotation of minerals using two kinds of collectors. In: Somasundaran P (ed.) *Fine Particle Processing*, American Institute of Mining, Metallurgical and Petroleum Engineers, New York, pp. 787–801.

Bubble–Particle Capture

J. Ralston, University of South Australia, The Levels, Adelaide, Australia

Copyright © 2000 Academic Press

Introduction

Bubble–particle capture is the heart of froth flotation. For efficient capture to occur between a bubble and a hydrophobic particle, they must *first* undergo a sufficiently close encounter, a process that is controlled by the hydrodynamics governing their approach in the aqueous environment in which they are normally immersed. Should they approach quite closely, within the range of attractive surface forces, the intervening liquid film between the bubble and particle will drain, leading to a critical thickness at which rupture occurs. This is then followed by movement of the three-phase-line contact line (the boundary between the solid particle surface, receding liquid phase and advancing gas phase) until a stable wetting perimeter is established. This sequence of drainage, rupture and contact line movement constitutes the *second* process of attachment. A stable particle–bubble union is thus formed. The particle may only be dislodged from this state if it is supplied with sufficient kinetic energy to equal or exceed the detachment energy, i.e. a *third* process of detachment can occur.

The capture (or collection) efficiency E of a bubble and a particle may be defined as:

$$E = E_C \times E_A \times E_S \qquad [1]$$

where E_C is the collision efficiency, E_A is the attachment efficiency and E_S is the stability efficiency of the bubble–particle aggregate. This dissection of capture efficiency into three parts was originally proposed by Derjaguin and Dukhin (1960–61) and focuses attention on the three zones of bubble–particle capture where, in order, hydrodynamic interactions, surface forces and forces controlling bubble–particle aggregate stability are dominant.

This article describes each of the substeps in the bubble–particle capture process. The individual processes and efficiencies are focused upon, since they provide the key to understanding the substeps. Our knowledge of the various efficiencies has been enhanced by six important publications, referred to in **Table 1**, each of which signalled major advances in our understanding and catalysed further research in this interdisciplinary field of colloid and flotation science.

Processes and Substeps

Process 1: Collision Efficiency

For a batchwise flotation process, the flotation recovery (the mass of particles recovered in a given time t) R is given by:

$$R = 1 - \exp - t\left(\frac{3GhE_CE_AE_S}{2d_bV}\right) = 1 - \exp(-tk) \qquad [2]$$

where G is the volumetric gas flow rate of a swarm of bubbles of diameter d_b passing through a particle suspension of volume V and depth h, and:

$$k = \frac{3GE_CE_AE_Sh}{2d_bV} \qquad [3]$$

The flotation rate constant k is directly analogous to that obtained in chemical reaction kinetics. Its value will be partly determined by the substep(s) in bubble–particle collision, attachment and detachment processes, as well as by physical variables such as G. (For a constant G and constant bubble size distribution, d_b will be an appropriate average.)

Equation [2] has been shown to apply, for example, to a system of monodisperse polystyrene latex particles floating under batchwise conditions. A plot of $\ln(1 - R)$ versus t yields the rate constant k. For systems that are polydisperse in particle size and/or in which particles of different hydrophobicities are present, the recovery then becomes the sum of a series of exponential terms and the plot of